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Short Communication

Applicability of electroanalysis for monitoring oxalic acid (OA) concentration during its electrochemical oxidation

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ABSTRACT

In the present paper, differential pulse voltammetry (DPV) techniques has been studied for monitoring of the concentration of oxalic acid (OA) during its electrochemical oxidation (EO) in acidic media at BDD anode applying a current of 60 mA cm^{-2}. Glassy carbon has been used for DPV measurements using two analytical procedures: calibration curves (DPV_{CC}) and standard addition method (DPV_{SAM}). DPV analyses have compared with classic titration method and HPLC achieving a good fit, confidence intervals and limits.

1. Introduction

Oxidative electrochemical technologies offer an alternative solution to many environmental problems in the process industry, because electrons provide a versatile, efficient, cost-effective, easily automatizable and clean reagent [1–6]. Nowadays, thanks to intensive investigations that have improved the electrocatalytic activity and stability of electrode materials and optimized reactor geometry, electrochemical technologies have reached a promising state of development and they can be effectively used for disinfection and purification of wastewater polluted with organic compounds [1–8]. As far as the nature of the organic substrate is concerned, it has been shown that carboxylic acids, common intermediates of the EO of several organic substrates, are rather stable and are mineralized at longer times [1,2,7]. In particular, for OA, last intermediate in electrochemical wastewater treatment processes.

The EO of OA has been extensively studied (as described by authoritative papers [1,2,9]), as a model reaction, somewhat at the border between organic and inorganic electrochemistry. Looking at this literature [9–21], the EO of OA or oxalate species have been monitored using different methods, such as liquid chromatography [9–14], gas chromatography [15,16], flow-injection catalytic spectrophotometry [17], ion exclusion chromatography [18] and enzymatic methods. However, these instrumental methods have some disadvantages such as high cost, low sensitivity, insufficient selectivity and long analysis times. Among them, the most used method is the $KMnO_4$ titrimetric analysis, being the cheapest way for quantifying OA [9,19–22], but this analytical method is time-consuming with low accuracy and affected by interferences from other species in solution.

In last decades, electroanalysis has attracted considerable research attention as an alternative for detecting, quantifying and monitoring the concentration of different organic and inorganic species; since these electrochemical methods offer high sensitivity and selectivity. For example, in the case of OA, few reports have used the electroanalytical techniques (ET) to determine it [23,24]. These studies deal with determination of OA in food by using two different electrode surfaces: multiwall carbon nanotubes (MWNTs) modified glassy carbon (GC) electrode and sensor based on the palladium nanoparticle-loaded carbon nanofiber (Pd/CNF) composites. Both studies have reported high selectivity and sensitivity for quantifying OA by employing electroanalysis. Both studies have reported high selectivity and sensitivity for quantify OA by employing electroanalysis.

For this reason, the aim of this work is to propose the applicability of ET for monitoring OA concentration, during its EO at BDD anode. The ET employed was DPV using glassy carbon (GC) electrode to quantify OA concentration by two different analytical

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procedures: calibration curves (DPV_{CC}) and standard addition method (DPV_{SAM}). Finally, the results obtained by DPV techniques were compared with the measurements achieved by traditional $KMnO_4$ titration and HPLC methods, in order to establish the confidence and error intervals.

2. Experimental

2.1. Reagents

Two solutions of OA (Vetec, dihydrate salt) were prepared in 0.5 mol L^{-1} H_2SO_4 (Vetec), using MilliQ water: (i) 0.1 mol L^{-1} (used for electroanalysis procedures as standard solution) and (ii) 0.15 mol L^{-1} (used for electrochemical oxidation experiments). The 0.1 mol L^{-1} $KMnO_4$ solution was prepared, and standardized by titration of a known amount of anhydrous and pure OA. Chemicals were of analytical grade, supplied by Vetec Company.

2.2. Analytical methods

During the EO tests, the OA concentration was determined by different analytical methods: conventional $KMnO_4$ titration using a $KMnO_4$ solution of 0.1 mol L^{-1}, HPLC and DPV measurements, but making use of two different analytical measurement procedures: calibration curves (DPV_{CC}) and standard addition method (DPV_{SAM}).

Electrochemical analyses were carried out by using Potentiostat/Galvanostat Autolab model PGSTAT320. DPV measurements were usually conducted in the potential window from 0.5 to 1.8 V in H_2SO_4 0.5 mol L^{-1}. The experiments were carried out at 25 °C with a conventional three-electrode system, and applying scan rate of 50 mV s^{-1}; equilibration time (s): 10; modulation time (s): 0.04; initial potential (V): 0.5; end potential (V): 1.8; step potential (V): 0.006; modulation amplitude (V): 0.04995 and standby potential (V): 0.05. A GC electrode with an exposed geometric area of ca. 0.5 mm^2 was used as the working electrode. A platinum wire and an Ag/AgCl (KCl 3 mol L^{-1}) were employed as the auxiliary and reference electrodes, respectively.

For DPV_{CC} procedure, calibration curve for OA was achieved, being obtained by evaluating the peak intensity as a function of the analyte concentration, and considering at least fourteen analyte concentrations. In the case of DPV_{SAM}, an electrolysis sample (1 mL) was put in 30 mL of H_2SO_4 0.5 mol L^{-1} supporting electrolyte, after that, by adding known volumes of the OA solution of 0.1 mol L^{-1} in the measuring vessel, the concentration of carboxylic acid remaining in the solution was quantified. Both procedures were achieved using DPV technique under experimental conditions described above.

Alternatively, the concentration of OA was detected and quantified by HPLC analysis with an Agilent 1100 LC equipped with an Agilent 1100 Series UV/vis detector set at λ = 210 nm. The LC was filled with a Luna 5u C-18 (150 mm × 4.6 mm, 5 μm) column at 30 °C. For these analyses, 20 μL samples were injected into the LC and a 25 mmol L^{-1} KH_2PO_4 solution of pH 2.5 (adjusted with H_3PO_4) at 1.3 mL min^{-1} was circulated as mobile phase.

2.3. Electrochemical oxidation of OA

Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 0.3 L, and the solution was stirred by a magnetic stirrer. The experiments of EO of OA were performed under galvanostatic conditions using a VERSTAT3 potentiostat/galvanostat (Princeton Applied Research) under acidic conditions (H_2SO_4 0.5 mol L^{-1}, for all experiments). The applied current density was established at 60 mA cm^{-2} due to higher removal efficiencies achieved in previous work [9]. Boron-doped diamond (BDD) thin-film electrode, supplied by Adamant Technologies (Switzerland), it was used as anode and Ti as cathode. Both electrodes were a plate with an area of 10 cm^2 and with one side only exposed to the solution and an inter-electrode distance of 1.5 cm.

3. Results and discussion

To estimate electrochemical characteristics of GC electrode and choose the working range of potentials, DPV curves were recorded in H_2SO_4 0.5 mol L^{-1} and in solutions containing OA. The working range of potentials was delimited from 0.5 to 1.7 V and the results are presented in Fig. 1A. As can be seen, in the absence of OA, no peak was observed (dashed line). However, in the presence of OA, an irreversible oxidation peak at ≅1.23 V (vs. Ag/AgCl) on the bare GC electrode was observed; attributed to EO of OA (filled lines). These experiments at the GC electrode showed that OA is electroactive at this material, its oxidation taking place about 300–400 mV before the oxygen evolution reaction (o.e.r) onset, ($HCO^-_{2(ads)} \rightarrow CO_2 + H^+ + e^-$) [9].

Data obtained analyzing OA standard solutions, in acidic media, allowed to point out a linear relationship existing between peak current and OA concentration (inset in Fig. 1A); these results at GC electrode highlights the advantages of this electrode device.

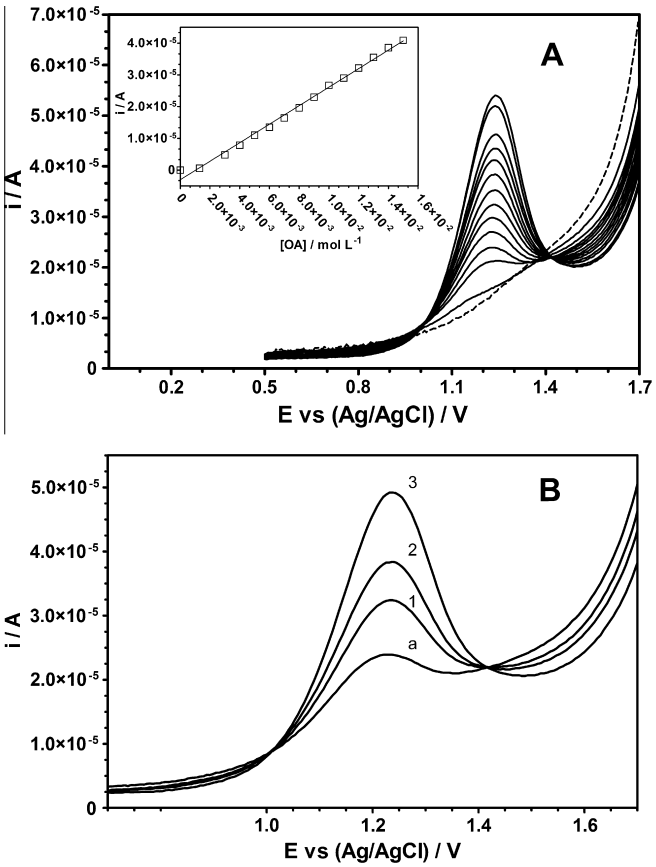

Fig. 1. (A) Differential pulse voltammograms obtained at 0.5 mol L^{-1} H_2SO_4 (as supporting electrolyte – dashed line) containing different concentrations of OA (2×10^{-3}; 3×10^{-3}; 4×10^{-3}; 5×10^{-3}; 6×10^{-3}; 7×10^{-3}, 8×10^{-3}; 9×10^{-3}; 1×10^{-2}; 1.1×10^{-2}; 1.2×10^{-2}; 1.3×10^{-2}; 1.4×10^{-2} and 1.5×10^{-2} mol L^{-1} – filled lines) using GCE. Inset: Linear dependence of the peak current on OA concentration. (B) Example of voltammograms relevant to the analysis of OA at GC electrode by successive standard additions; (curve a) sample and (curves 1–3) successive standard additions: 2×10^{-3}; 3×10^{-3} and 4×10^{-3} mol L^{-1} of OA.

From above results, calibration curve for OA was created (inset Fig. 1A), by evaluating the peak intensity as a function of the analyte concentration, and considering at least fourteen analyte concentrations. The analysis of residuals from the linear regression proved that a linear response exists from 2×10^{-3} to 1.5×10^{-2} M, with regression coefficients always larger than 0.999 [25]; however, the results also evidenced a little variability of slopes and intercepts, which can be due to differences in the actual status of the electrode surface.

A preliminary estimation of the Limits of Detection, LOD, was also possible by using the approach based on the standard deviation of regression:

$$\mathrm{LOD} = 3 \times \frac{S_{\frac{y}{x}}}{b} \quad (1)$$

where $S_{\frac{y}{x}}$ is the residual standard deviation and b is the slope of the calibration plot. On the basis of the results obtained, in this specific case, a LOD of about 5.1×10^{-4} M was estimated.

On the other hand, in the case where the samples of analyte were analyzed by DPV_{SAM}, an electrolysis sample (1 mL) was put in 30 mL of supporting electrolyte (curve a, Fig. 1B), after that, by adding known volumes of the OA solution of 0.1 mol L^{-1} in the measuring vessel (curves 1, 2 and 3, Fig. 1B), the concentration of carboxylic acid remaining in the solution was quantified.

Fig. 1B shows an example of the voltammograms relevant to one of these calibrations. The responses allowed estimating the four values of I_{know} (one value at each known volume) to be used for obtaining the slope and the intercept, analyte concentration = $[OA_{unknown}]$, of the functional relationship between the standard deviation of the response variable. After that, the $[OA_{unknown}]$ will be estimated by ordinary linear least square regression. The results showed at both analytical procedures confirm the advantages of sensor for monitoring OA concentration by DPV method using GC electrode, which improves the sensitivity and selectivity to determine the concentration of OA during EO experiments.

The applicability of the DPV for the monitoring of OA concentration has been verified during the EO with BDD anode at 60 mA cm^{-2}. During the electrolyses samples were withdrawn and analyzed by DPV methods, titration with permanganate and HPLC to quantify the remaining concentration in the solution. The evolution of OA concentration obtained with the different techniques has been reported in Fig. 2. As can be observed, the EO behavior observed at both DPV methods is very similar; showing a modest discrepancy between OA concentrations determined by both ET and HPLC. However, based on HPLC results, we can assume that the titration measurements showed a notorious discrepancy respect to the DPV methods.

As strongly suggested by other authors [25], the analytical procedures were performed by maintaining the analytical system under statistical control conditions by estimating the statistical error. Thus, the error obtained during the measurements of OA concentration using DPV procedures and $KMnO_4$ titration was calculated as:

$$\mathrm{Error}\,(\%) = \frac{OA_{HPLC} - OA_{measured}}{OA_{HPLC}} * 100 \quad (2)$$

where OA_{HPLC} is the concentration of OA determined with HPLC and $OA_{measured}$ is the concentration of OA determined with DPV procedure or titration method.

As it can be seen in Fig. 3, the DPV_{CC} gave reliable results than DPV_{SAM}. However, both DPV procedures achieved lower statistical error than that observed by titration method. From inset on Fig. 3, we can assume that the DPV_{CC} method has achieved a statistical error below 5% in 80% of all responses accomplished as well as it is important to evidence that the OA average value estimated from all responses lies in the OA_{HPLC} expected. Alternately, the OA concentration results estimated by DPV_{SAM} lie between 20% of statistical error, showing an OA average value about 10%; and this error fit-well within of consent instrumental error. Conversely, the titration measurements showed an asymmetrical behavior, exhibiting higher statistical error and standard deviation respect to HPLC results. It is important to remark that, based on existing literature [19], OA electrosorption on anode surface is an important pre-requisite for its EO, without participation of hydroxyl radicals at some electrode materials. Conversely, at BDD anode, no OA adsorption is attained, due to "non-active" nature of this electrode, but the organic oxidation clearly involves intermediates that are only available during the oxygen evolution reaction (hydroxyl radicals) [26,27]. In addition, electrolysis using BDD anodes in aqueous media, containing sulphate ions, generates peroxodisulphates ($2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$) on BDD surface [27,28]. Consequently, these oxidants could have some significance on analytical results obtained by DPV procedures.

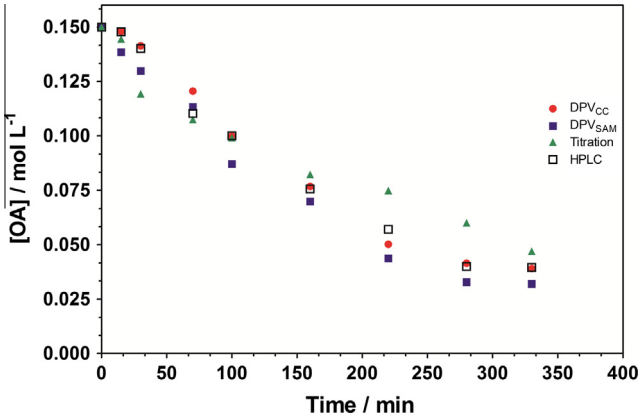

Fig. 2. Comparison between traditional $KMnO_4$ titrimetry, DPV analysis and HPLC for quantifying OA concentration during its electrochemical degradation at BDD anode. Experimental conditions: $[OA]_0$ = 0.15 mol L^{-1}, 60 mA cm^{-2} and 25 °C.

Finally, restricting now our analysis to DPV procedures, both ET were surprisingly better than hoped; allowing their use with acceptable confidence, quantification precision and good sensitivity.

4. Conclusions

DPV methods, using GC as working electrode seem to offer a fast, reliable, economic and simple way for determining OA during

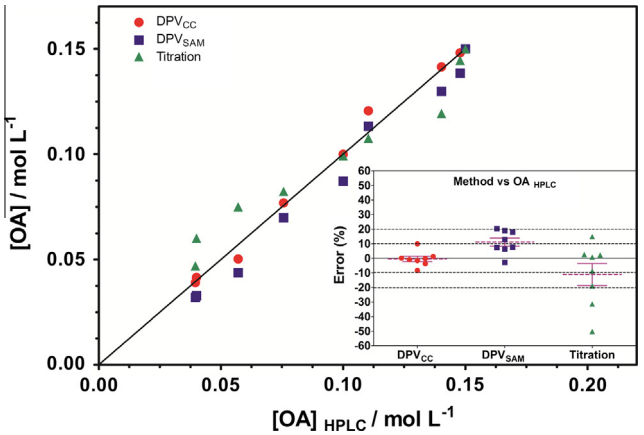

Fig. 3. Comparison of measurements performed using ET and titration respect to HPLC results expected. Inset: statistical error, mean and standard deviation for each technique, focusing the dispersion data.

its EO. The sensor is characterized by a higher sensitivity and reproducibility and the low limit of detection allows reducing matrix effects by working in highly diluted solutions. The difference between OA concentration determined with DPV_{CC} and HPLC was below 10% but this method is cheaper than the commonly used chromatography analysis and than other instrumental methods involving more toxic or expensive reagents. However, it is important to remark that the sensitivity of GC sensor would be improved via surface modification, as reported by other authors [23,24]. At present, our results demonstrate the potential of these ET for future applications in environmental, chemical and biological monitoring sensors. Finally, further experiments are being developed in order to study the EO of OA using other supporting electrolyte and electrocatalytic materials (Pt, graphite, Au, PbO_2) employing ET as a monitoring technique and these results will be published in a future paper.

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